AIAA-2000-5345

PROCESSING OF CARBON NANOTUBES FOR REVOLUTIONARY SPACE APPLICATIONS[1]

Bradley S. Files, NASA Johnson Space Center, Houston, TX

Extraordinary properties of carbon nanotubes are being examined for applications in advanced materials. This activity focuses on developing this new technology for use in spaceflight. Johnson Space Center's role in this project is to bridge the gap between the basic science of nanotubes and engineering applications. Recent work in the processing of nanotube composites has clarified several specific issues that will be discussed in this paper. Single wall carbon nanotubes are produced, purified, and finally added to polymers to fabricate a composite. Previous experience with graphite and carbon black composites is combined with new tools and techniques for nanoscale materials to try to make a revolutionary material.

INTRODUCTION

Ultimately, all advanced space exploration activities are driven by weight concerns for launch vehicles and space systems. Interplanetary exploration by humans will only be possible by decreasing the mass of each necessary system. Radical new technologies are requisite for lowering the overall vehicle mass to something that is realistic for implementation of long duration missions. Johnson Space Center (JSC) has chosen to pursue enabling technologies that may produce revolutionary breakthroughs in mass reduction for space missions. For almost four years JSC has studied properties of nanotubes and nanotube composites for use in space exploration.

The Nobel Prize winning discovery of the buckyball in 1985 at Rice University[1] has led to the ultimate fiber for lightweight reinforcement, the single walled carbon nanotube. The structure of a carbon nanotube is similar to a graphene sheet, wrapped back onto itself with a diameter near a nanometer. It has been shown that single wall nanotubes (SWNTs) have extraordinary mechanical, electrical, and thermal properties.[2] By fabricating materials on the atomic level, strength properties can be realized beyond what was previously dreamed possible. SWNTs are known to be 10-100 times stronger than steel at a sixth the weight.[3] If a significant portion of this strength can be translated from the nanoscopic fiber to a macroscopic material, nanotubes will revolutionize the aerospace industry. The application of nanotubes within polymer matrix composites as a new "bottom-up" method for fabrication of aerospace materials offers significant system level benefits such as multifunctional materials which are not only the structural elements, but also provide tailorable conductivity for dissipation of static energy for spacecraft, efficient thermal management, and possible micrometeoroid protection. Nanotubes without a matrix also are being pursued in NASA's collaboration with Rice University. Rice's method for aligning nanotubes in a magnetic field opens up new possibilities for manufacturing advanced materials.[4]

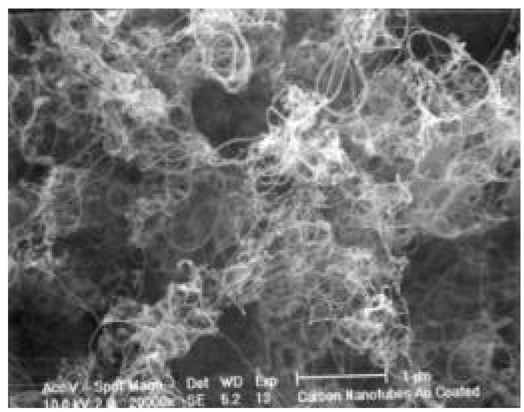

Figure 1: As-produced single wall carbon nanotube material produced at JSC. These ropes consist of 10-100 tubes per bundle, in random tangles.

Our work centers on producing multifunctional materials for use in space applications. As a first step we have concentrated on extracting the inherent mechanical properties of nanotubes to make useful structures on a macroscopic scale.[5] In addition to having a strength ten times higher than any of today's engineering materials, nanotubes exhibit a strain-to-failure above five percent. This combination of strength, stiffness, and toughness will open a new field of materials science. Preliminary work on nanotube-enhanced polymer fabrication has proven difficult due to the high surface area and chemical resistance of nanotubes. Manipulation of nanotubes is also a difficult task without many tools for assembling nanoscopic materials. SWNTs are generally formed as bundles, and dispersion of the individual tubes out of the bundles is an important focus of our work.

Single-wall carbon nanotubes have mechanical, electrical, and thermal properties that make them likely candidates as the ultimate reinforcement for space applications. These applications are not only the main structural members of spacecraft. They may also include fabrics for micrometeoroid debris protection, advanced space suits, or inflatable structures. Sensor, battery, and nanoelectronics applications of nanotubes are also current pursuits of NASA centers. Research in the area of nanotube structural and thermal materials is ongoing at Johnson Space Center, including active collaboration with NASA centers, other branches of government, academia, and industry.

APPLICATIONS

As nanotubes become more readily available, applications studies will be pushed forward by research efforts that use their mechanical, electrical, and thermal properties. By incorporating nanotubes into polymers and other materials, the nanoscopic properties can be translated to a macroscopic level. The pursuit of this goal is the reason that the field of nanotube technology is growing rapidly, even though only small quantities of the tubes now exist.

The focus of our research group is in the areas of structural materials, thermal management materials, electrically conductive materials, and energy storage. Using nanotubes as the filler in a composite can provide an advantage over today's materials. This advantage could be based on a single property or the combination of several nanotube properties, resulting in a multifunctional material. Research in carbon nanotubes themselves is still in the early stages, but early work in materials applications will provide a basis for further development as the technology matures.[6]

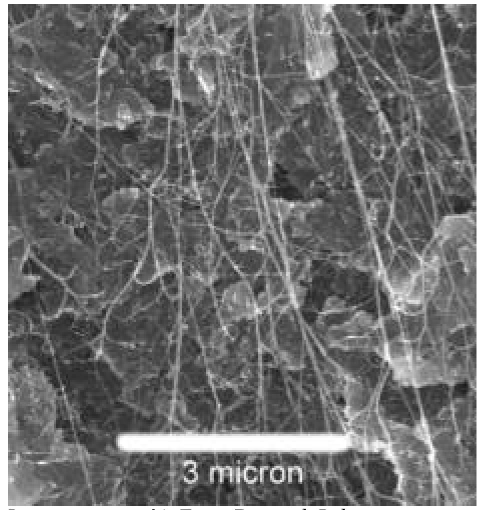

Image courtesy Air Force Research Lab

Figure 2: Nanotube epoxy composite sample entirely fabricated at Johnson Space Center. Nanotubes have pulled out of the fracture surface from the opposite side.

Many other applications of nanotubes are of interest to NASA, and some of these are being developed at Ames Research Center and other NASA centers. As the basic science and chemistry are better understood, new areas of interest are found. So many possibilities exist for this technology that collaboration between groups is necessary to best utilize all the known properties and behaviors.

Several issues exist regarding implementation of nanotube applications. Many of these are based around production and manipulation of the tubes. For the past several years the best methods of production have resulted in gram quantities per day of material which contains large amounts of impurities. Also, the chemistry of nanotubes must be developed to the point where they can interface properly with other materials. This includes any necessary purification of the raw material, dispersion of the individual tubes from the naturally-forming bundles, and possible chemical functionalization. Because of the scale of these materials, a new toolbox of characterization techniques is required. This is mostly a matter of using equipment in a new way, to study properties on the nanoscopic scale. Each of these items is a key to preparing nanotubes to be used for a wide range of applications.

CONTROLLED GROWTH

An ongoing problem in the nanotube field has been the lack of a bulk production method. Recent advances in this area give reason for optimism that current gas-phase processes may be scaled up to make significant quantities of material.[7] At the same time these new methods may also make much purer material. Previous production processes resulted in raw material that must be put through labor-intensive multi-step treatments before they may be clean enough to be used in applications.[8] Once the answers have been found to making large amounts of mostly pure nanotubes, the next step will be to control the production in terms of diameter, length, and chirality.

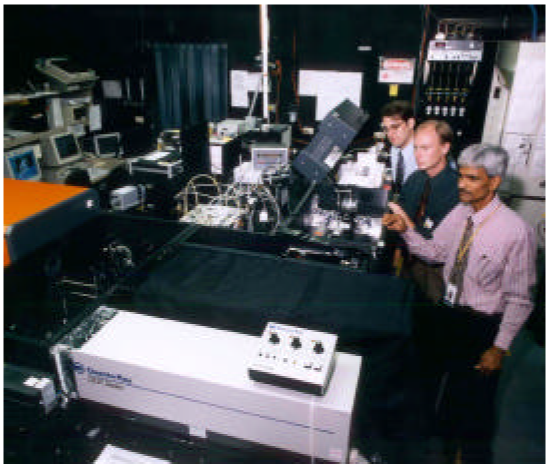

Figure 3: William Holmes, Brad Files, and Sivaram Arepalli examine the laser production apparatus.

Different applications require different sizes and types of nanotubes, based on how they will be used. For example, a sensor application may not need large quantities of tubes, but it may require one or more with specific chemical or electrical properties. Or sometimes an array of fibers may need to all have similar properties, which are dependent on the chirality and diameter. For structural materials applications the nanomechanics is not yet well understood, so the critical length of the fibers is not known. Also, it is not trivial to find the average length of a batch of nanotubes. Therefore, it is quite possible that the fibers that are currently available may not be long enough to achieve load transfer across the fiber/matrix interface. If this turns out to be the case, then methods for producing longer nanotubes could become a high priority.

Understanding the nanotube growth process is the best route for eventually growing specific sizes and types. By using spectroscopic methods, the plasma plume in the laser ablation process can be probed to measure nanotube precursors and catalysts both temporally and spatially during a production run.[9] This information is then distributed to the scientific community to build on the knowledge base and help demystify the production process. Hopefully, this will help to expand the possibilities for producing the specific type of desired tubes. Then they can be modified as desired and used in applications based what is necessary.

It should be mentioned that although our work consists mostly of single-wall carbon nanotubes, other nanotubes might better suit a particular application. In some cases multi-wall tubes may be adequate, and they are currently more readily available and less expensive. As methods are proven to produce boron nitride[10] and other types of nanotubes, more options will be available with varied chemical, electrical, thermal, structural, and optical properties. Although single-wall carbon nanotubes may be the best material for some purposes, scientists should also consider other nanofibers as the options increase.

NANOTUBE CHEMISTRY

Extensive research in the chemistry of nanotubes is essential for expanding their possibilities in applications. Simply using raw material from commercial sources without chemical modification usually gives results that are less than expected. Individual tubes tend to form large bundles, or ropes, of 10-100 tubes each. This greatly decreases the available surface area, which can be important for gas or energy storage. Chemistry methods can be used to disperse these bundles into individual tubes, purify the raw material, and chemically modify them before being put into applications.

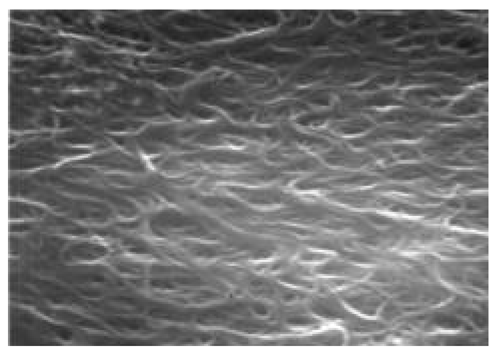

Figure 4: Single wall carbon nanotubes after purification, filtered down to the form of a "Buckypaper". These tubes were produced by the laser ablation process at JSC.

So far much work has been necessary to try to purify the raw material from the production system. Most processes result in only 10-50% nanotubes, with the rest being amorphous or graphitic carbon and metal catalyst particles. Purification procedures often include acid refluxing, oxidation, and filtration steps, or a combination of these. Each step can eliminate some amount of impurities in the sample, but the process can be quite long, and each step causes some nanotubes to be lost or destroyed. Better purification techniques are necessary unless new methods are able to produce high quality as predicted. If these procedures result in material with only 5% or less impurities, then purification may become a trivial step. However, this purification chemistry has been important over the last several years.

Single wall nanotubes coming out of the production apparatus are arranged in bundles, with many individuals lined up like a rope configuration. For most applications, these tubes must be separated from the bundles so that a gas, liquid, or solid can interact with as much surface area as possible. For gas and energy storage applications, the usefulness of the material is directly related to the amount of surface available for interactions. In the case of structural materials, it has been shown that the tensile strengths of nanotube bundles relate inversely to their diameter. Small bundles allow for most of the fibers to interact with a matrix, and the possibility for strengthening greatly increases due to the increase in bundle strength. Tubes are attracted to each other by Van der Waals forces, so this must be overcome when trying to separate them. A number of possibilities exist, including types of chemical derivatization of the tubes or wrapping the tubes with polymer chains to decrease tube-tube interactions. At very low concentrations of tubes in solvents, sonication can cause enough of a disturbance to pull the tubes apart. However, this approach has limited success as concentration is increased to reasonable levels. Nanotube dispersion has not been well studied until recently, as the importance of this issue has become more obvious.

Possibilities for chemical modifications of nanotubes are endless. Both end and sidewall derivatization are believed to serve important roles, depending on the modification desired. The simplest functionalization route appears to be attaching chemical groups to either endcaps or open ends. It has been shown that the sides of the tubes may be modified, including addition of fluorine atoms to open up many more options for attachment. Which modification is necessary depends on the interaction that is needed for a specific application. For structural materials the keys would be improved interaction with a matrix and minimal degradation of mechanical properties. For gas storage use the key might be to increase the possibility of attracting a specific gas, while the change in tube structure in this case may not be important. In the near term chemical functionalization methods should be developed across a wide range of possible needs. Then as specific needs are found, unique modifications can expand on those techniques that have already been developed. One possibility would be to use functionalization of the tubes to help assemble or orient them as desired, working toward self-assembly of large arrays. Assembly and chemical manipulation methods could make the difference in how quickly nanotube applications become a reality.

CHARACTERIZATION TECHNIQUES

One of the most difficult challenges in the nanotube field is to figure out what is present in a given sample. Then, after making a modification you want to figure out what has changed. In going from the macroscopic to the nanoscopic, these seemingly simple questions become riddles, often perplexing the best scientists. A full suite of tools is needed to answer questions such as the percent yield of nanotubes versus impurities in a sample. Current methods for this include Raman spectroscopy,[11] thermogravimetric analysis (TGA), and visually by SEM and TEM. Each of these gives an idea of the purity of a sample, but each only shows part of the answer, with more questions remaining.

Size and type or chirality of the tubes are important pieces of information, and this can be dependent on the method of production. Determining how these differences come about from the production methods could help show what the growth mechanisms are. But researchers are still working on procedures for finding diameter, length and chirality distribution in a sample. Diffraction methods appear to give some good information, and AFM and STM can add to the overall knowledge, but it is possible that tubes are being selectively removed for examination. Therefore, the sample may not be representative of the bulk material.

Chemical characterization techniques are even trickier, because of the incomplete information that comes from methods such as IR spectroscopy. Some groups report success in finding chemical signatures of endcap or sidewall derivatization, while others have failed to duplicate these results. We do know that these characterization tools are one key to opening the frontier of nanotechnology. Without proper methods for examining the material at this level, uncertainty can prevail in terms of what exists and how it has been modified.

FUTURE DIRECTIONS

Each of the previous sections addresses a current concern in working toward applications with carbon nanotubes. Growth, chemistry, and characterization are all important steps in the process of fabricating advanced composites, energy storage devices, sensors, or other applications which are now only in our imagination. These keys to the future of the nanotube field will open the door for more eventual uses, provided that the scientific foundation is sound.

In an area of future importance such as nanotube technology, it is advantageous to promote collaborations between industry, academia, and government agencies. This path will provide the best use of resources for all involved and will benefit those who work together.

REFERENCES

1. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature*, **318**, 162-163, (1985).
2. B. I. Yakobson and R. E. Smalley, *American Scientist*, **85**, 324-337, (1997).
   B. S. Files and B. M. Mayeaux, *Advanced Materials and Processes*, **156**, 47-49, (1999).
3. M-F Yu, B. S. Files, S. Arepalli, and R. S. Ruoff, *Physical Review Letters*, **84**, No. 24, 5552-5555, (2000).
   D. A. Walters et al., *Appl. Phys. Lett.*, **74**, 3803, (1999).
4. D. A. Walters, NanoSpace2000 Conference Presentation, Houston, TX, (2000).
5. B. S. Files, *Journal of Nanoparticle Research*, **1**, 507-509, (1999).
6. P. Calvert, Nature, **399**, 210, (1999).
   L. S. Schadler et al., *Appl. Phys. Lett*., **73**, 3842-3844, (1998).
7. P. Nikolaev et al., *Chemical Physics Letters*, **313**, 91, (1999).
8. T. Guo, P. Nikoaev, A. Thess, D. T. Colbert, R. E. Smalley, *Chemical Physics Letters*, **243**, 49, (1995).
   A. G. Rinzler et al., *Applied Physics A*, **67**, 29, (1998).
   C. Journet et al., *Nature*, **388**, 756, (1998).
9. S. Arepalli, P. Nikolaev, W. Holmes and C. D. Scott, *Applied Physics A*, **70**, 125-133, (2000).
   S. Arepalli and C. D. Scott, *Chemical Physics Letters*, **302**, 139-145, (1999).
10. D. P. Yu et al., *Applied Physics Letters*, **72**, No. 16, 1966-1968, (1998).
11. M. Iliev, A. P. Litvinchuk, S. Arepalli, P. Nikolaev and C. D. Scott, *Chemical Physics Letters*, **316**, 217-221, (2000).